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COMPLETE SPECIFICATION

Process for the Preparation of Epoxide Resins

We, HENKEL & CO G.M.B.H., a German Company, of 67, Henkelstrasse, Duesseldorf-Holthausen, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a new and especially advantageous process for the preparation of hardenable compounds containing epoxide groups which can be hardened with all substances hitherto proposed as hardeners for epoxide resins.

It is known that hardenable compounds containing epoxide groups can be prepared by reacting polyhydric phenols or cyanuric acid with a haloepoxyalkane, e.g. epichlorhydrin, or with a suitable dihalo compound, e.g. dichlorhydrin, in aqueous or alcoholic solution in the presence of alkali. Polyhydric phenols have also already been reacted with epichlorhydrin to give the corresponding chlorhydrin ethers and the latter have then been converted into hardenable compounds containing epoxide groups by splitting off hydrogen halide by means of alkali. The technical operation of this process is not simple because, among other things, the inorganic salt formed, e.g. sodium chloride, must either be washed out with water or removed by filtration, which generally causes difficulties. The product must subsequently be freed from organic solvent or from water by heating in a vacuum.

It has now been found that hardenable compounds containing epoxide groups can be prepared in a more simple manner than before by reacting organic compounds, which contain in the molecule more than one phenolic hydroxyl group e.g. polyhydric phenols with a haloepoxyalkane which contains a halogen atom adjacent to the epoxy group, at elevated

temperature in the presence of high molecular weight catalysts insoluble in the reaction mixture.

The haloepoxyalkane is used in an amount of more than two mol for each phenolic hydroxyl group. Organic high molecular weight compounds insoluble in the reaction mixture, which contain either

(a) saltlike groups, i.e. a salt group which is bound to a molecular radical, or

(b) groups which under the reaction conditions is changed into saltlike groups, or

(c) acid amide groups, are added as catalysts. In order to isolate the epoxide compounds formed, the catalyst is separated from the reaction mixture. Then the excess haloepoxyalkane and volatile products of the reaction which are formed are distilled off.

Organic compounds which contain in the molecule more than one phenolic hydroxyl group and which may be used as starting substances for the process according to the invention are, for example, polyhydric phenols such as resorcinol, hydroquinone, 1,4-dihydroxynaphthalene and other isomeric dihydroxynaphthalenes, 4,4'-dihydroxydiphenyl, 2,2'-dihydroxydiphenyl and other isomeric dihydroxydiphenyls, 4,4'-dihydroxydiphenylmethane, 4,4'-dihydroxydibenzyl, and also substituted dihydroxydiphenylmethanes such as are formed by acid condensation of phenols with aldehydes or ketones, especially 4,4'-dihydroxydiphenyl-2,2-propane, the so-called diphenylpropane or bisphenol A which can be prepared from phenol and acetone, and in addition dihydroxydiphenylcyclohexane and others.

The polyhydric phenols used as starting substances may contain other substituents or functional groups in the molecule in addition to the phenolic hydroxyl groups, for example,

hydrocarbon residues, ether groups, ester groups, halogen atoms, hydroxyl groups and others, provided that the reaction is not thereby interfered with. Thus, for example, compounds such as 4,4'-dihydroxybenzophenone and other isomeric dihydroxybenzophenones, 4,4'-dihydroxydiphenylsulphone and its isomers, as well as halogenated derivatives of the above-mentioned phenols, e.g. of diphenylolpropane are suitable as starting substances. Esterification or etherification products of polyhydric phenols which still contain free phenolic hydroxyl groups may also be used, for example, the esters from 1 mol of phthalic acid and 2 mol of resorcinol, hydroquinone or diphenylolpropane. Derivatives of aromatic hydroxycarboxylic acids may likewise be employed, for example esters of salicylic acid or p-hydroxybenzoic acid with polyhydric alcohols, such as ethylene glycol-bis-p-hydroxybenzoic acid ester.

In addition to the phenolic hydroxyl groups the starting substances may also contain a carboxyl group, which also reacts with the haloepoxyalkane under the conditions employed. Such compounds are, for example, 4,4-bis-(4-hydroxyphenyl)-pentanoic acid, which can be prepared by acid condensation of 1 mol of levulinic acid with 2 mol of phenol. No protection is claimed within the scope of the present application for the reaction with compounds which contain more than one carboxyl group in the molecule. Further suitable starting substances are compounds which contain more than two phenolic hydroxyl groups in the molecule, for example pyrogallol or 2,2,3,3-tetrakis-[4'-hydroxyphenyl]-butane or condensation products from substituted or unsubstituted phenols with formaldehyde or other aldehydes or ketones, especially the so-called Novolaks or Resols. Compounds of more or less than high molecular weight are obtained according to the molecule size of these latter starting substances.

The foregoing list of compounds suitable as starting substances is not exhaustive. A full list of the compounds in question may be found, for example, in the book "Epoxide compounds and epoxide resins" by A. M. Paquin, published by Springer, 1958, pages 256-307.

Haloepoxyalkanes which contain a halogen atom adjacent to the epoxy group and which are reacted according to the invention with the above-described compounds containing in the molecule more than one phenolic hydroxyl group are, for example, epichlorhydrin, epibromhydrin, 1,2-epoxy-3-chlorobutane, 1-chloro-2,3-epoxybutane, 1-chloro-2,3-epoxy-5-methoxypentane and others. Epichlorhydrin is used as the preferred starting material. The technical epichlorhydrin usual in the trade with a water content of about 0.1% may be used without purification or drying,

The amount of haloepoxyalkane should be more than 2 mol per phenolic hydroxyl group. It is advantageous to employ the haloepoxyalkane in substantially greater excess, e.g. 5-40 mol or more per phenolic hydroxyl group. The unreacted haloepoxyalkane is not changed during the reaction and may easily be recovered and used again.

As catalysts, substances which do not dissolve in the reaction mixture and which therefore can easily be mechanically separated after the reaction has ended, are used. In this way there is avoided the necessity for freeing the reaction product from the catalyst by the troublesome method of washing out, or the undesired side reactions caused by catalyst residues when the volatile constituents of the reaction mixture are distilled off. Therefore organic high molecular weight compounds which are insoluble in the reaction mixture are preferably used as catalysts. Suitable catalysts are first of all those compounds which contain saltlike groups, e.g. the salts of high molecular weight organic acids such as alkali metal, ammonium or amine salts of polyacrylic acid. It is particularly suitable to use the so-called ion exchange resins as catalysts. Cation exchange resins which may contain acid groups, e.g. sulphonic acid groups, carboxyl groups, phosphoric acid groups and others, are used for the process according to the invention in the form of their salts, e.g. in the form of the alkali metal, ammonium or amine salts. It is also possible to use as catalysts anion exchange resins, i.e. ion exchangers containing basic groups, e.g. amino groups, quaternary ammonium or phosphonium groups, as well as ternary sulphonium groups, in the form of their salts, e.g. in the form of the chlorides or sulphates.

A further group of suitable catalysts comprises high molecular weight compounds which contain reactive groups which under the conditions used may be converted into saltlike groups. Such compounds are, for example, high molecular weight organic bases, e.g. anion exchangers in the form of the free bases. Other resins which contain basic nitrogen atoms, which as is known may be converted with epihalohydrins into quaternary compounds, are also suitable, e.g. melamine resins or epoxide resins hardened with organic amines. In addition, high molecular weight compounds are suitable which contain divalent sulphur atoms which, with haloepoxyalkanes, are capable of being transformed into ternary sulphonium compounds.

Furthermore, high molecular weight organic compounds which contain acid and basic groups together in the molecule are suitable as catalysts. Such products are, for example, on the market as ion exchangers under the designation amphoteric ion resins. Obviously the so-called mixed base ion exchangers, i.e.

mixtures of anion and cation exchangers, may also be used.

Finally, compounds which contain acid amide groups, e.g. polyamides such as nylon, casein or wool, and also the known urea resins, are suitable as catalysts.

The said catalysts are suitably used in granular form for the process according to the invention. Finely powdered portions are advantageously separated beforehand by sieving and/or washing out. In this way, the separation of the catalyst from the reaction mixture, e.g. by centrifuging, decanting or filtering, is carried out extraordinarily smoothly. A coarse filter suffices for the filtration. A narrow mesh wire sieve is advantageously used for this purpose.

In general, the catalysts may be used as often as desired, since, apart from a small amount of mechanical abrasion, they are not consumed. If their activity should fall after using for a number of times, they may be regenerated in a simple manner. The type of regeneration depends upon the chemical constitution of the catalyst concerned. In many cases washing and soaking with water is sufficient. In other cases the catalysts are regenerated by treatment with salt solutions or with dilute acids or bases. A certain amount of water contained in the catalysts does not generally adversely affect the reaction according to the invention.

The quantity of the catalyst may vary within wide limits. The optimum quantity depends upon the constitution of the catalyst and may be easily found from case to case by preliminary experiments.

The process according to the invention is carried out by heating the said starting substances and the catalyst for a few hours. The reaction temperature in general lies above 60° C. Temperatures over 200° C. should be avoided as a rule. In some cases it is expedient to add an inert organic solvent to the reaction mixture. When epichlorhydrin, which is especially suitable, is used as the haloepoxyalkane, and in a relatively large excess, it is advisable to boil the reaction mixture under reflux. The catalyst is then separated by, for example, passing the mixture through a fine sieve made of V4A wire. This sieve is fine enough to retain the catalysts, but has no special features. The separation of the catalyst proceeds extraordinarily smoothly and rapidly in this way. The excess haloepoxyalkane and the volatile reaction products, e.g. dichlorhydrin, are then distilled off, preferably under reduced pressure. Small quantities of water, which may be present in the reaction mixture when water-containing catalysts or commercial epichlorhydrin are used, are removed herewith, so that the reaction product is water-free. The haloepoxyalkane distilled off may be used for further charges, if necessary after suitable purifica-

tion. Dihalohydrin formed can easily be converted into epihalohydrin in known way.

The hardenable compounds containing epoxide groups prepared according to the process of the invention are, according to their chemical constitution, principally ethers of epoxy alcohols, especially glycidic. Since they contain more than one epoxide group in the molecule, they are hardenable. The new products are not identical with the epoxide resins prepared by known processes, e.g. from diphenylolpropane and epichlorhydrin in aqueous-alkaline solution. They differ from these as a rule by a higher content of organically-bound halogen, e.g. chlorine. They are also distinguished by a lower viscosity and a lighter colour compared with the products obtained by the known processes.

The products according to the invention may be hardened with all compounds presently known to be suitable as hardeners for epoxide resins, for example, with organic bases or with di- or poly-carboxylic acids or their anhydrides. They can be applied in many ways as already known in the art or described in the literature. For example, in conjunction with suitable hardeners, they can be used as adhesives, casting resins, lacquer resins or for the preparation of laminated material or synthetic materials for reinforcing glass fibres. Quite generally, the new products may be used for all those purposes for which the use of epoxide resins has previously been proposed. Owing to their advantageous properties, especially their lower viscosity and their lighter colour, they are in many cases superior to the previous epoxide resins for these purposes. By bleaching with small quantities, up to 1% by weight of organic peroxides, e.g. methyl ethyl ketone peroxide or cyclohexanone peroxide, water-white products are obtained without difficulty.

An increase in the content of epoxide oxygen and a decrease of the halogen content of the products according to the invention can be achieved in various ways, for example, by working with a large excess of the haloepoxyalkane concerned or by treating a resin prepared by the present process again with epichlorhydrin and catalyst. In this way products can be obtained whose compositions approach those of simple glycidic ethers of the phenols in question. In some cases even practically pure glycidic ethers may be obtained.

Hardenable compounds containing epoxide groups with widely differing contents of epoxide oxygen can be prepared by the process according to the invention, and in this way the properties of the products may be varied to a considerable extent. If, for example, value is placed on a particularly short hardening times, then as a rule a product with a high content of epoxide oxygen is used. If, on the other hand, a long period of process-

ing of the resin-hardener mixture is desired, resins with a smaller content of epoxide oxygen are chosen. The elasticity of the hardened products can also be varied by the content of epoxide oxygen of the resins. Further possibilities of variation are given by the choice of starting substances and by addition of plasticising compounds.

EXAMPLE 1.

- 10 110 g of hydroquinone, 3700 g of commercial epichlorhydrin (water content about 0.1%) and 80 g of a water-containing commercial anion exchanger Dowex 1×10 (Registered Trade Mark) were heated for 5½ hours under reflux with stirring. The product was then filtered from the catalyst. The filtrate was freed from excess epichlorhydrin at about 40 mm Hg. The residual volatile constituents were distilled off at 0.5 mm Hg until the temperature of the distilling liquid was 100° C. 220 g of a waxlike substance remained which largely crystallised after standing for a little at room temperature. The product had the following characteristics:—
- 25 Epoxide oxygen - - - 12.9%
Chlorine: - - - 1.6%
Molecular weight: - - - 230
- Dowex 1×10 consists of a strongly basic anion exchanger based on polystyrene, which contains quaternary benzyl-ammonium groups. This ion exchanger was used with the same result in the form of the free base and in the form of the hydrochloric acid salt.

Stability of form according to Martens
(German Industry Standards 53, 458)

81° C.

Impact toughness

(German Industry Standards 53, 453)

6 to 8 cm.kg/cm³

Brinell hardness

German Industry Standards 57, 302)

1620 kg/cm²

50 g of the epoxide resin prepared according to the foregoing example were stirred with 0.5 g of methylisobutylketone peroxide and allowed to stand at 50° C. for 24 hours. The

bleaching effect obtained resulted in the following colour values:—

Colour according to Lovibond (1" tray)
(diluted with acetone 1:1)

Starting material	after 12 hours	after 24 hours
2.7 yellow	1.0 yellow	0.4 yellow
0.9 red	0.2 red	0.1 red

- 10 g of the epoxide resin prepared by the foregoing example were mixed at 100° C. with 4 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride. Hard aluminium strips 100 mm in length, 20 mm broad and 2 mm in thickness were glued together with this mixture with simple overlapping of 10 mm, and hardened at 140° C. for 14 hours. The test bodies thus prepared had the following tensile shearing strengths at different temperatures:—

Temperature	Tensile shearing strength
at 25° C.	2.8 kg/mm ²
at 100° C.	2.5 kg/mm ²
at 150° C.	1.9 kg/mm ²
at 200° C.	0.2 kg/mm ²

To determine the tensile shearing strengths given above, an apparatus was used such as is used for the determination of the tensile strength of plastic substances according to German Industry Standards 53, 371.

EXAMPLE 2.

110 g of resorcinol, 3700 g of commercial epichlorhydrin and 80 g of water-containing Dowex 1×10 were heated for 5 hours under reflux with stirring. After removal of the catalyst and the excess epichlorhydrin, 200 g of a product of boiling point 150–162° C./0.15 mm. were obtained from the resulting residue by fractional distillation at a pressure of 0.15 mm Hg; the product consisted principally of pure resorcinol diglycid ether.

EXAMPLE 3.

228 g of bisphenol A, 3700 g of commercial epichlorhydrin and 80 g of water-containing Dowex 1×10 were reacted and worked up as described in Example 1. 360 g of a resin with the following characteristics were obtained:—

Epoxide oxygen - - - 5.8%
Chlorine - - - 5.3%
Viscosity at 50° C. - - - 8600 cp
(measured with the Hoeppler viscometer)

Colour according to Lovibond
(1" tray) - - - 2.7 yellow, 0.9 red
(diluted with acetone in the proportion 1:1)

100 g of this resin were melted and mixed with 50 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride at 100° to 110° C. Test samples were prepared from this mixture which, after hardening at 150° C. for 14 hours, provided the following results:—

EXAMPLE 4.

366 g of tetrachlorobisphenol A (4,4'-di-hydroxy - 3,3',5,5' - tetrachlorodiphenyl - 2,2-propane), 5550 g of epichlorhydrin and 100 g of a water-containing Dowex 1×10 were reacted and worked up as described in Example

1. 480 g of a resin with the following characteristics were obtained:—

Epoxide oxygen - - - - 5.0%

Chlorine - - - - 29.1%

Viscosity at 50° C. - - - 17000 cp

Colour according to Lovibond

(1"-tray) 4.6 yellow, 0.6 red
(diluted with acetone in the proportion 1:1)

10 g of the epoxide resin prepared according to the foregoing example were mixed at 100° C. with 3 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride. Hard aluminium strips 100 mm in length, 20 mm in breadth and 2 mm in thickness were glued together with this mixture by simple overlapping of 10 mm, and hardened at 140° C. for 14 hours. The test bodies prepared in this way gave the following tensile shearing strengths at different temperatures:—

Temperature	Tensile shearing strength
25° C.	1.9 kg/mm ²
100° C.	2.4 kg/mm ²
150° C.	2.0 kg/mm ²
200° C.	0.5 kg/mm ²

EXAMPLE 5.

286 g of 4,4-bis-(4-hydroxyphenyl)-penta-noic acid, prepared by acid condensation of 1 mol of levulinic acid and 2 mol of phenol, were heated for 8 hours under reflux with 3.7 kg of commercial epichlorhydrin (water content about 0.1%) and 200 g of a water-containing commercial anion exchanger (Lewatit—Registered Trade Mark—MN in the form of the sulphuric acid salt Lewatit MN is a strongly basic polycondensate which contains —NR₃⁺ groups). The reaction mixture was worked up in the manner described in Example 1. 440 g of an epoxide resin were obtained which had the following characteristics:—

Epoxide oxygen - - - - 6.5%

Chlorine - - - - 5.5%

Viscosity at 50° C. - - 24000 cp

Lewatit (Registered Trade Mark) MN is a strongly basic polycondensate which contains —NR₃⁺ groups.

From 100 g of this resin and 40 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride, test bodies were prepared in the same way as described in Example 3, by means of which the following test results were obtained:—

Stability of form according to Martens

105° C.

Impact toughness 6 to 8 cm. kg/cm²

Brinell hardness 1400 kg/cm²

10 g of the epoxide resin prepared according to the foregoing example were mixed at 100° C. with 3 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride. Hard aluminium strips 100 mm in length, 20 mm in breadth and 2 mm in thickness were glued together with this mixture by simple overlapping of 10 mm, and hardened at 180° C. for 4 hours. The test bodies prepared in this way gave the following tensile shearing strengths at different temperatures:—

Temperature	Tensile shearing strength
25° C.	2.75 kg/mm ²
100° C.	3.30 kg/mm ²
200° C.	1.20 kg/mm ²

A further sample of 10 g of the resin prepared according to the above example was mixed with 5 g of a commercial polyamide containing free amino groups (commercial product Versamid—Registered Trade Mark—140 of the General Mills Co.). Hard aluminium strips 100 mm in length, 20 mm in breadth and 2 mm in thickness were glued together with this mixture by simple overlapping of 10 mm, and hardened at room temperature for 48 hours. After this the test bodies had a tensile shearing strength of 2.2 kg/mm².

EXAMPLE 6.

42 g of pyrogallol were heated for 10 hours under reflux with stirring with 1850 g of commercial epichlorhydrin (water content about 0.1%) and 100 g of a water-containing Lewatit (Registered Trade Mark) MN in the form of the free base. The reaction mixture was worked up in the manner described in Example 1. 80 g of a light coloured epoxide resin were obtained which had 6.9% of epoxide oxygen.

EXAMPLE 7.

114 g of diphenylolpropane were heated for 7 hours under reflux with stirring with 1850 g of commercial epichlorhydrin (water content about 0.1%) and 200 g of water-containing Lewatit—Registered Trade Mark—S 100 in the form of the ammonium salt. Lewatit—Registered Trade Mark—S 100 is a styrene resin which contains —SO₃H groups on the nucleus and is strongly acid. The reaction mixture was worked up in the manner described in Example 1. 170 g of an epoxide resin with 5.7% of epoxide oxygen were obtained.

Two similar charges, but using the sodium salt and the potassium salt instead of the ammonium salt, provided the same results.

EXAMPLE 8.

114 g of diphenylolpropane were heated for 7 hours under reflux with stirring with 1850 g of commercial epichlorhydrin and 200 g of a commercial melamine resin hardened for 5 hours at 120° C. and which was in the form

of a granulate of particle size 0.3 to 1.0 mm. The reaction mixture was worked up in the manner described in Example 1. 176 g of an epoxide resin with 5.9% of epoxide oxygen were obtained. (The melamine resin above-mentioned was prepared by condensation of 1 mol melamine with 3 mols formaldehyde in the form of a 30% aqueous solution at a pH of 8-8.5 and a temperature of 80° C. to a precipitation number of 1:1, that is to say, to a point where the turbidity just occurred on dilution of the resin solution with the same quantity of water. The product was dried to powder on a heated roller).

EXAMPLE 9.

90 g of tetrachlorodiphenylolpropane were

Stability of form according to Martens
(German Industry Standards 53, 458)

90° C.

Impact toughness

(German Industry Standards 53, 453)

4 to 6 cm. kg/cm²

Brinell hardness

German Industry Standards 57, 302)

1610 kg/cm²

EXAMPLE 10.

55 g of tetrabromo-diphenylolpropane were heated for 7 hours under reflux with stirring with 550 g of epibromhydrin and 80 g of the anion exchanger Dowex 1×10 in the form of the hydrobromic acid salt. The reaction mixture was worked up in the manner described in Example 1. 71 g of an epoxide resin which contained 3.0% of epoxide oxygen and 53.1% of bromine were obtained. The resin was light in colour.

EXAMPLE 11.

25 g of 4,4'-dihydroxydiphenylsulphone (diphenylolsulphone) were heated for 10 hours under reflux with 600 g of epibromhydrin and 300 g of nylon in the form of small cubes (commercial product Zytel—Registered Trade Mark—of Du Pont). The reaction mixture was worked up in the manner described in Example 1. 65 g of an epoxide resin with 4.8% of epoxide oxygen and 13.4% of bromine were obtained.

EXAMPLE 12.

The following example shows that the ion exchanger used is also active in the absence of water.

4000 g of commercial epichlorhydrin and 100 g of Lewatit (Registered Trade Mark) MN (water-containing) were heated at the boil while stirring in a distillation apparatus. The heating was continued until water could no longer be detected in the distillate passing over. At this point the temperature in the distillation vessel was 117° C. Altogether 123 g of distillate passed over.

The dehydrated mixture, after addition of 228 g of diphenylolpropane, was heated for 6 hours under reflux with stirring. The mixture was then worked up in the manner

heated for 7 hours under reflux with 1150 g of commercial epichlorhydrin and 62 g of an epoxide resin hardened for 4 hours at 180° C. with benzidine and prepared according to Example 3 of the present application (proportion of resin to hardener 2:1), in powder form with stirring. The reaction mixture was worked up in the manner described in Example 1. 128 g of an epoxide resin with 5.5% of epoxide oxygen were obtained.

100 g of this resin were melted with 40 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride and hardened in moulds for 14 hours at 140° C. The test bodies prepared in this way gave the following values:—

described in Example 1. 364 g of an epoxide resin were obtained which contained 5.4% of epoxide oxygen.

EXAMPLE 13.

135 g of tartaric acid were dissolved in 150 g of a 40% aqueous formaldehyde solution with stirring and heating to 40° C. 195 g of phenol were then added at 60° C. The mixture was slowly heated to boiling. At about 100° C. internal temperature a lively reaction set in. The mixture was then heated under reflux for a further 15 minutes. After cooling, the lower layer was washed three times with dilute ammonia solution, stirred into 3 litres of cold water and left to stand overnight. After pouring off the aqueous phase, the remaining resin was taken up in 200 c.c. of acetone and freed from volatile fractions in a vacuum at 0.5 mm Hg up to a temperature of 85° C. in the distillation vessel. 192 g of a yellow brittle Novolak resin were obtained.

50 g of this resin were dissolved in 1850 g of epichlorhydrin (water content about 0.1%). The solution was heated together with 100 g of water-containing Lewatit (Registered Trade Mark) MN in the form of the free base for 8 hours under reflux with stirring. The reaction mixture was then worked up in the manner described in Example 1. 72 g of a very light-coloured epoxide resin were obtained which contained 6.95% of epoxide oxygen.

50 g of this epoxide resin and 25 g of a hardener consisting of 75% of phthalic anhydride and 25% of tetrahydrophthalic anhydride were melted together at 100° C. and well mixed. Test samples were prepared from this mixture which, after hardening at

140° C. for 14 hours, had the following properties:—

Stability of form according to

	Martens	111° C.
5	Impact toughness	5 to 6 cm. kg/cm ²
	Brinell hardness	1615 kg/cm ²

With the same resin-hardness mixture as described above, hard aluminium strips of 100 mm in length, 20 mm in breadth and 2 mm in thickness were glued together with simple overlapping of 10 mm, and hardened at 140° C. for 14 hours. The test samples so prepared had the following tensile shearing strengths at different temperatures:—

15	Temperature	Tensile shearing strength
	20° C.	1.9 kg/mm ²
	100° C.	2.2 kg/mm ²
	200° C.	2.0 kg/mm ²

20 EXAMPLE 14

58 g phloroglucinol, 1850 g epichlorohydrin (water content 0.2%) and 80 g of the anion exchanger Lewatit (Registered Trade Mark) MN in the form of hydrochloride were heated for 8 hours under reflux with stirring. As described in Example 1, the reaction mixture was worked up. 120 g of a light epoxide resin were obtained, which contained 9.0% epoxide oxygen and 6.4% chlorine.

30 WHAT WE CLAIM IS:—

1. Process for the preparation of epoxide resins, in which organic compounds which contain in the molecule more than one phenolic hydroxyl group and one or no carboxyl group are reacted at elevated temperature with a haloeпоxyalkane, which contains a halogen atom adjacent to the epoxy group, said haloeпоxyalkane being used in an amount of more than 2 mol per phenolic hydroxyl group, in the presence of a catalyst consisting of an organic high molecular weight compound insoluble in the reaction mixture, said catalyst containing either

- 45 (a) a saltlike group, or
(b) a group which is converted into a saltlike group under the reaction conditions, or

(c) an acid amide group, and, after separation of the catalyst, excess haloeпоxyalkane and volatile reaction products which have been formed are distilled off and if desired the product obtained is hardened in known way.

2. Process as claimed in Claim 1, in which the haloeпоxyalkane is epichlorohydrin.

3. Process as claimed in either Claim 1 or 2, in which the quantity of haloeпоxyalkane used lies within the range 5—40 mol to each phenolic hydroxyl group.

4. Process as claimed in any of Claims 1—3, in which the catalyst is an ion exchange resin.

5. Process as claimed in Claim 4, in which the ion exchange resin is a cation exchange resin in the form of a salt, preferably the alkali metal, ammonium or amine salt.

6. Process as claimed in any of Claims 1—4, in which the catalyst is an anion exchange resin in the form of the free base or in the form of a salt.

7. Process as claimed in any of Claims 1—4, in which the catalyst is an amphoteric ion resin.

8. Process as claimed in any of Claims 1—3, in which the catalyst is an aminoplast, especially a melamine or urea resin.

9. Process as claimed in any of Claims 1—3, in which the catalyst is an epoxide resin hardened with a basic hardener.

10. Process as claimed in any of Claims 1—9, in which the catalyst is used in granular form and finely powdered portions are previously separated.

11. Process as claimed in any of Claims 1—10, in which the reaction product is bleached by the addition of organic peroxides.

12. Process for the preparation of epoxide resins substantially as described with reference to any one of the Examples 1—14.

13. Epoxide resins when prepared in accordance with the process as claimed in any of the preceding claims.

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